

VII. Additivity of Free Energy Changes; Coupled Reactions

A. Free energy changes are additive. If



then

$$\Delta G_3 = \Delta G_1 + \Delta G_2$$

B. Since free energy changes are additive, it is possible to bring about a nonspontaneous reaction by coupling it with a reaction for which ΔG° is a large negative number.

SELF-TEST**A. Multiple Choice:**

1. For a certain reaction, the standard free energy change is -70.0 kJ at 100 K and -40.0 kJ at 200 K. For this reaction

- | | |
|------------------------------------|------------------------------------|
| a. $\Delta H > 0$; $\Delta S > 0$ | b. $\Delta H > 0$; $\Delta S < 0$ |
| c. $\Delta H < 0$; $\Delta S > 0$ | d. $\Delta H < 0$; $\Delta S < 0$ |
| e. need more information | |

2. How many of the following statements are true at 25°C and 1 atm?

- ΔH_f° of $\text{H}_2(\ell) = 0.0$ kJ
- ΔH_f° of $\text{H}^+(\text{aq}) = 0.0$ kJ
- S° of $\text{H}_2(\text{g}) = 0.0$ kJ
- S° of $\text{H}^+(\text{aq}) = 0.0$ kJ

- a. 0 b. 1 c. 2 d. 3 e. 4

3. If the value of ΔG° does not change with temperature and pressure, this would mean that

- | | |
|---|-------------------|
| a. ΔH has a positive or negative value. | b. $\Delta H = 0$ |
| c. ΔS has a positive or negative value. | d. $\Delta S = 0$ |

4. Consider the following chemical processes.

- (1) $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$
- (2) $\text{C}(\text{s}) + \text{H}_2\text{O}(\ell) \rightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$
- (3) $3\text{Fe}(\text{s}) + 4\text{H}_2\text{O}(\text{g}) \rightarrow 4\text{H}_2(\text{g}) + \text{Fe}_3\text{O}_4(\text{s})$
- (4) $2\text{Ag}(\text{s}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{AgCl}(\text{s})$
- (5) $2\text{NO}_2(\text{g}) \rightarrow 2\text{O}_2(\text{g}) + \text{N}_2(\text{g})$

The entropy change, ΔS° is expected to be positive in

- a. (1),(2) b. (1),(3) c. (2),(3) d. (2),(4) e. (2),(5)

5. For a dissociation reaction
- $\Delta S < 0$
 - $\Delta S = 0$
 - $\Delta S > 0$
 - ΔS depends on the equilibrium constants.
 - none of the above is true.
6. Which of the following statements is *always* true?
- An exothermic reaction is spontaneous.
 - A reaction for which ΔS° is positive is spontaneous.
 - If the number of moles of gas does not change in a chemical reaction, then $\Delta S^\circ = 0$.
 - If ΔH° and ΔS° are both positive, then ΔG° will decrease when the temperature increases.
7. For the sublimation of dry ice,
- $$\text{CO}_2 (\text{s}) \rightarrow \text{CO}_2 (\text{g})$$
- the signs of ΔH° and ΔS° should be
- $\Delta H^\circ > 0$; $\Delta S^\circ > 0$
 - $\Delta H^\circ < 0$; $\Delta S^\circ < 0$
 - $\Delta H^\circ > 0$; $\Delta S^\circ < 0$
 - $\Delta H^\circ < 0$; $\Delta S^\circ > 0$
 - need more information
8. Increasing the temperature at which a reaction takes place will have the greatest effect on
- ΔG°
 - ΔS°
 - ΔH°
 - $\Delta H^\circ / \Delta S^\circ$
9. As observed in the real world about us, each of the following processes is spontaneous except
- dissolving salt in water.
 - rusting of an iron nail.
 - formation of the elements from boiling water.
 - combustion of gasoline.
10. Pick the best statement.
- The free energy change is independent of temperature.
 - The entropy of a substance is independent of temperature.
 - The entropy change of a reaction is independent of temperature.
 - The enthalpy of a substance is independent of temperature.

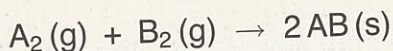
B. True or False:

- _____ 1. The second law of thermodynamics states that in a spontaneous process there is a net increase in entropy, taking into account the system and the surroundings.
- _____ 2. Energy is conserved in chemical reactions.
- _____ 3. The enthalpy change for spontaneous reactions is always negative.
- _____ 4. The free energy change for a reaction that increases in entropy is always positive.
- _____ 5. If ΔG is 0, then $\Delta S = \Delta H$.
- _____ 6. ΔS for a reaction between two gases to produce a liquid is negative.
- _____ 7. When a liquid freezes, its entropy increases.
- _____ 8. Spontaneous reactions always occur rapidly.
- _____ 9. As is true with enthalpies, absolute entropy values cannot be determined.
- _____ 10. At 0 K, a perfect crystal has $S = 0$.

C. Less than, Equal to, Greater than

Answer the questions below, using **LT** (for *is less than*), **GT** (for *is greater than*), **EQ** (for *is equal to*), or **MI** (for *more information required*) in the blanks provided.

The reaction given below takes place in a cylinder which feels warm to the touch after the reaction is complete.



- _____ 1. At all temperatures, ΔS° _____ 0.
- _____ 2. At all temperatures, ΔH° _____ 0.
- _____ 3. At all temperatures, ΔG° _____ 0.
- _____ 4. S° for $\text{AB}(\ell)$ _____ S° for $\text{AB}(\text{s})$.
- _____ 5. ΔH_f° for $\text{A}_2(\text{g})$ at 25°C and 1 atm _____ 0.

D. Problems:

Consider methanol (CH_3OH).

1. Write the equation for the combustion of two moles of methanol with oxygen into carbon dioxide and liquid water.
2. Calculate ΔH° for the reaction.
3. Calculate ΔS° for the reaction.
4. Calculate ΔG° for the reaction at 25°C .
5. Calculate ΔG° for the reaction at 100°C .

6. At which temperature (if any) will the reaction be spontaneous?

7. Calculate the boiling point of methanol if $\Delta H_{\text{vap}}^{\circ} = 37.95 \text{ kJ}$ and $\Delta S_{\text{vap}}^{\circ} = 112.9 \text{ J/K}$.

8. Calculate ΔG at 25°C when $P_{\text{CO}_2} = 730 \text{ mm Hg}$ and $P_{\text{O}_2} = 1.1 \text{ atm}$.

ANSWERS**Exercises:**

(E1) The house being built

(E2) Before the game

(E3) The team after the huddle

(E4) $\Delta H_f^\circ = -1762 \text{ kJ/mol}$; $S^\circ = 184.4 \text{ J/K}$

(E5) $\Delta H^\circ = 28.1 \text{ kJ}$; reaction endothermic; $S^\circ = 108.7 \text{ J/K}$; increase in entropy;
 $\Delta G^\circ = -4.3 \text{ kJ}$; reaction spontaneous

(E6) 413 K

(E7) any temperature $< 1772 \text{ K}$

(E8) (1) $4\text{H}^+ (\text{aq}) + \text{MnO}_2 (\text{s}) + 2\text{Cl}^- (\text{aq}) \rightarrow \text{Mn}^{2+} (\text{aq}) + 2\text{H}_2\text{O} + \text{Cl}_2 (\text{g})$
(2) 23.4 kJ (3) 113 kJ

(E9) $\Delta G^\circ = 16 \text{ kJ}$; nonspontaneous

Self-Test**A. Multiple Choice:**

1. d

2. c

3. d

4. e

5. c

6. d

7. a

8. a

9. c

10. c

B. True or False:

1. T

2. T

3. F

4. F

5. F

6. F

7. F

8. F

9. F

10. T

C. Less than, Equal to, Greater than:

1. LT

2. LT

3. MI

4. GT

5. MI

D. Problems:

1. $2\text{CH}_3\text{OH} (\ell) + 3\text{O}_2 (\text{g}) \rightarrow 2\text{CO}_2 (\text{g}) + 4\text{H}_2\text{O} (\ell)$

2. $\Delta H^\circ = -1452.8 \text{ kJ}$

3. $\Delta S^\circ = -161.8 \text{ J/K}$

4. $\Delta G^\circ = -1404.6 \text{ kJ}$

5. $\Delta G^\circ = -1392.4 \text{ kJ}$

6. any temperature below 8979 K

7. 336.1 K

8. -1405.5 kJ